COMBINATION OF INDIRECT MEASUREMENTS TO IMPROVE SIGNAL ESTIMATION IN POLYMER CHARACTERIZATION

G. L. FRONTINI* and G.E. ELIÇABE
Facultad de Ingeniería. Universidad Nacional de Mar del Plata.
Instituto de Investigación en Ciencia y Tecnología de Materiales (INTEMA).
Juan B. Justo 4302 (7600) República Argentina.
e-mail: gfrontin@fi.mdp.edu.ar

Keywords: Regularization; inverse problem; indirect measurements; material characterization; Particle-Size-Distribution

Abstract

A form to combine two kinds of indirect measurements to be processed together is proposed for ill-conditioned problems. Linear individual measurements with unknown proportionality constants jointly considered determine a unique non-linear problem. To solve this problem a method that includes in a single step the recovery of the signal and the calculation of the regularization parameter according to the Generalized Cross Validation technique is proposed. In order to investigate the convenience of simultaneous versus individual processing, a set of synthetic experiments performed on suspensions of polystyrene particles is analyzed. The results clearly show that when the data are jointly processed the quality of the Particle Size Distribution estimated is highly superior. This work shows that simultaneous processing of experimental data from different sources seems to be a valid alternative to improve the quality of indirect measurements.

1. Introduction

The aim of this work is to develop a methodology to process simultaneously two different kinds of indirect measurements of an unknown signal, in order to produce a unique estimation, with less error than that obtained processing any of the given measurements separately. The case where the relation between the unknown signal and the measured function is linear is considered. The additional uncertainty of having an unknown parameter related to the relative nature of the measurements is also taken into account.

The situation described above may appear in the problem of determining the Particle Size Distribution (PSD) of a polymer latex. Turbidimetry and Elastic Light Scattering (ELS) are two popular techniques used to determine sizes of suspended particles in the range between 100 nm and several micrometers. Recent technological improvements in laboratory equipment made possible to readily obtain turbidity and ELS spectra for a range and number of wavelengths and angles, not commonly attainable in the past using standard laboratory equipment. The information contained in these spectra can be related through Mie theory (van de Hulst, 1981; Kerker, 1969; Bohren and Huffman, 1983) to the PSD of the sample of dispersed particles analyzed.

Turbidity at several wavelengths was used in Eliçabe and García Rubio (1989; 1990) to determine the PSD of polystyrene latex. The size distribution was estimated by solving a linear inverse problem in which the turbidity determinations and their model were incorporated. The wavelengths used in those references were between 200 and 900 nm. In that range the technique can be used to characterize particles of diameters from 50 nm to several micrometers. However, not in all cases the refractive index of the particles is well known in that whole range of wavelengths. In polymers, the refractive index at the lower end (200 – 300 nm) of the wavelength range is normally not known because of the presence of absorption in that region. This effect limits the use of the whole set of measurements to those corresponding to wavelengths larger than 300 nm. This limitation reduces the resolution of the recovered PSD at the lower end of the diameter axis as shown in Eliçabe and García Rubio (1989).

The problem of obtaining the PSD from ELS measurements using Mie theory was treated in Glatter et. al (1985) for homogeneous spherical particles in general, and applied by Hofer et. al. (1989) for the determination of the PSD of oil-water emulsions. Again, a linear inverse problem was solved to estimate the size distribution. Using ELS it is possible to demonstrate, in the Rayleigh-Debye-Gans approximation, that there exists an upper value for the maximum diameter that can be found without error by an ideal scattering experiment. Therefore, lack of resolution for the larger diameters may be expected in this case. This result is discussed in Eliçabe and Frontini (1996).

From the previous paragraphs it can be concluded that, in general, a recovered distribution from turbidity data will be more unstable at the lower end of the diameter range, whereas a distribution obtained from ELS data will be more unstable at the higher end of the diameter range. This is clearly shown in Eliçabe and Frontini (1996) where turbidity and ELS are

* Author to whom correspondence should be addresed

compared in that respect. Therefore it is expected that the concurrent use of both techniques should improve the accuracy of the estimated distribution.

This idea was explored in a previous publication (Eliçabe and Frontini, 1996) in which it was demonstrated that it is possible to take advantage of the complementary characteristics of both techniques. In that publication turbidity and ELS determinations for a given sample were processed independently and properly combined. It was shown that the predicted undesirable effects suffered by the recovered distributions from the individual experiments could be greatly reduced when both experiments are processed together. However in that work, it was implicitly assumed that the ratio of scattered intensity to incident intensity, $I_s(\theta)/I_i$, can be precisely determined, and that all proportionality constants relating the measurements with the theoretical models such as: i) distance from sample to detector in ELS and ii) optical path length in turbidity, are also well known. Thus the combination procedure, developed under those restrictions, resulted in the formulation of a linear inverse problem.

The measurement of both incident and scattered intensities in the same experimental setup is not easy. The experiment could be conducted by measuring intensity at zero angle without the sample and, after swinging the detector arm to the desired angle, measuring it again with the sample in place. The main problem to be encountered is that I_i may be thousands of times greater than $I_s(\theta)$ and then appreciable errors are likely to occur because of the lack of detector linearity over such a range. The distance from the sample to the detector, r, in ELS, and the optical path length, l, in turbidity are parameters that have to be determined through calibration.

In this work, to avoid the determination of $I_s(\theta)/I_i$, r and l, the models to be used to estimate the PSD are assumed to have unknown proportionality constants independent of angle for ELS, and of wavelength for turbidity. This assumption gives to the proposed combination technique a more realistic basis. The problem to be solved to recover the PSD is not a linear inverse problem anymore, but it becomes a non-linear one. To solve this problem a method that includes in a single step the recovery of the PSD and the calculation of the regularization parameter according to the Generalized Cross Validation (GCV) technique (Golub et. al.,1979) is proposed. The method is demonstrated using a set of synthetic experiments generated with distributions of different characteristics.

2. Theory

If in an extinction experiment performed on a sample of thickness l of suspended particles, $I_i(\lambda_o)$ is the intensity at the light source and $I_t(\lambda_o)$ is the intensity at the light detector, then the attenuation experienced by the beam of light traversing the sample is defined as $\ln[I_t(\lambda_o)\ I_i(\lambda_o)]$. This quantity, also known as turbidity $\tau(\lambda_o)$, can be related to a function of the wavelength of the incident light in vacuum λo, for spherical particles with number PSD, $f(D)$, using Mie scattering theory (Bohren and Huffman, 1983) as follows,

$$\tau(\lambda_0) = \ln\left(\frac{I_t(\lambda_0)}{I_i(\lambda_0)}\right) = k_\tau \int_0^\infty Q_{ext}(\lambda_0, D) D^2 f(D) dD \quad [1]$$

$$\lambda_{0_{min}} < \lambda_0 < \lambda_{0_{max}}$$

In Eq [1] $Qext(\lambda_o,D)$ is the extinction efficiency of a particle of diameter D at λ_o and $k_\tau = l\ \pi/4$. Upper and lower limits for λ_o (λ_{omax}, λ_{omin}) are considered.

A similar equation can be obtained, using Mie theory (Bohren and Huffman, 1983), to relate the sample light scattering, $Is(\theta)$, at different angles θ, with its PSD:

$$I(\theta) = \frac{I_s(\theta)}{I_s(\theta_0)} = k_i \int_0^\infty S_{11}(\theta, D) f(D) dD \qquad \theta_{min} < \theta < \theta_{max} \quad [2]$$

Where $S_{11}(\theta, D)$ is the (1,1) element of the corresponding amplitude scattering matrix and

$$k_i = \left(\int_0^\infty S_{11}(\theta, D) f(D) dD \right)^{-1}$$

Upper and lower limits for θ (θ_{max}, θ_{min}) are also considered. This kind of relative measurements are easy to make and are the type most commonly reported in angular light scattering determinations. A single determination of $D_s(\theta) = K\ Is(\theta)$ could be used, in which case k_i would be equal to $\frac{K I_i \lambda_0^2}{(2\pi n_0 r)^2}$,

where n_o is the refractive index of the suspending medium and K is the instrument calibration constant.

Two sets of measurements [$\tau(\lambda_{0i})\ i=1, \ldots, n_1$ and $I(\theta_i)\ i=1, \ldots, n2$] are considered. If these measurements are grouped, two vectors can be defined:

$$\boldsymbol{\tau} = [\tau(\lambda_{o_1})\tau(\lambda_{o_2}) \cdots \tau(\lambda_{o_{n_1}})]^T \quad [3]$$

$$\mathbf{i} = \left[I_m(\theta_1) I_m(\theta_2) \cdots I_m(\theta_{n_2})\right]^T \quad [4]$$

The discrete versions of Eqs [1] and [2] can be written in general as:

$$\boldsymbol{\tau} = k_{\boldsymbol{\tau}}\mathbf{A}_{\boldsymbol{\tau}}\mathbf{f} + \mathbf{e}_{\boldsymbol{\tau}} = k\mathbf{A}_{\boldsymbol{\tau}}\mathbf{f}_r + \mathbf{e}_{\boldsymbol{\tau}} \qquad [5]$$

with $\mathbf{e}_{\boldsymbol{\tau}} \sim \mathrm{F}(\mathbf{0}, \mathbf{I}\sigma_{\boldsymbol{\tau}})$

and

$$\mathbf{i} = k_i\mathbf{A}_i\mathbf{f} + \mathbf{e}_i = \mathbf{A}_i\mathbf{f}_r + \mathbf{e}_i \qquad [6]$$

with $\mathbf{e}_{\mathbf{i}} \sim \mathrm{F}(\mathbf{0}, \mathbf{I}\sigma_{\mathbf{i}})$

where $\mathbf{f} = \left[f(D_1)\, f(D_2) \cdots f(D_m)\right]^T$, $\mathbf{f}_r = k_i\,\mathbf{f}$, $k = k_\tau/k_i$

and e_τ, e_i are error vectors with zero mean and covariance matrix $\mathbf{I}\sigma_\tau$ and $\mathbf{I}\sigma_i$ respectively. F stands for some density distribution of two parameters. These errors are in part due to quadrature and in part to measurement noise. A_τ and A_i are quadrature matrices calculated in the examples below as in Eliçabe and García Rubio (1990), using the software provided in the book of Bohren and Huffman (1983) to calculate $S_{11}(\theta,D)$ and $Qext(\lambda_o,D)$. The diameter axis was discretized in *m* points. Note that fr and k in Eqs [5] and [6] are the unknown variables.

When Eqs [5] and [6] have to be solved together, a proper normalization must be performed to take into consideration the different magnitudes of the involved variables. Assume that the errors in Eqs [5] and [6] are such that (other alternatives could be also handled),

$$\frac{\boldsymbol{\sigma}_{\boldsymbol{\tau}}}{\boldsymbol{\tau}_m(\boldsymbol{\lambda}_{0_i})_{max}} = \frac{\boldsymbol{\sigma}_{\mathbf{i}}}{I_m(\boldsymbol{\theta}_i)_{max}} = \boldsymbol{\sigma} \qquad [7]$$

If Eqs. [3] and [4] are normalized using the maximum values of τ and $\mathbf{i}$, i.e., $\boldsymbol{\tau}(\boldsymbol{\lambda}_{o_i})^{(max)}$ and $I(\theta_i)^{(\max)}$, the combined equation can be written as:

$$\mathbf{g} = \begin{bmatrix}\mathbf{g}_1\\ \mathbf{g}_2\end{bmatrix} = \begin{bmatrix}\boldsymbol{\tau}/\boldsymbol{\tau}(\boldsymbol{\lambda}_{o_i})^{(max)}\\ \hline \mathbf{i}/I(\boldsymbol{\theta}_i)^{(max)}\end{bmatrix} = \underbrace{\begin{bmatrix}k\mathbf{A}_{\boldsymbol{\tau}}/\boldsymbol{\tau}(\boldsymbol{\lambda}_{o_i})^{(max)}\\ \hline \mathbf{A}_{\mathbf{i}}/I(\boldsymbol{\theta}_i)^{(max)}\end{bmatrix}}_{\mathbf{a}(k,\mathbf{f}_r)} + \underbrace{\begin{bmatrix}\mathbf{e}_{\boldsymbol{\tau}}/\boldsymbol{\tau}(\boldsymbol{\lambda}_{o_i})^{(max)}\\ \hline \mathbf{e}_{\mathbf{i}}/I(\boldsymbol{\theta}_i)^{(max)}\end{bmatrix}}_{\mathbf{e}} \qquad [8.a]$$

with

$$\begin{bmatrix}\mathbf{e}_{\boldsymbol{\tau}}/\boldsymbol{\tau}(\boldsymbol{\lambda}_{o_i})^{(max)}\\ \hline \mathbf{e}_{\mathbf{i}}/I(\boldsymbol{\theta}_i)^{(max)}\end{bmatrix} \sim F(\mathbf{0}, \mathbf{I}\boldsymbol{\sigma}) \qquad [8.b]$$

where $\mathbf{I}\sigma$ is the covariance matrix of the normalized errors.

$\mathbf{f}_r$ and *k* can be estimated by solving the following non-linear minimization problem:

$$\underset{k,\mathbf{f}_r}{Min}\ \Phi(k,\mathbf{f}_r) = \{\left|\mathbf{g} - \mathbf{a}(k,\mathbf{f}_r)\right|^2 + \boldsymbol{\gamma}\,\mathbf{f}_r^T\mathbf{K}^T\mathbf{K}\mathbf{f}_r\} \quad [9]$$

where $\mathbf{K}^{\mathbf{T}}\mathbf{K}=\mathbf{H}$ is the regularization matrix selected in most cases as in Eliçabe and García Rubio (1990). The second term in Eq [9], that contains the regularization matrix, is needed as it is in the linear case, to regularize the solution which in all cases would be unstable without it because of the ill-posed nature of the original equations (Eqs [1] and [2]).

If *k* were known, the problem would be linear and would have the well known analytical solution due to Phillips (1962)

$$\hat{\mathbf{f}}_r = \left(\mathbf{A}^T\mathbf{A} + \boldsymbol{\gamma}\mathbf{H}\right)^{-1}\mathbf{A}^T\mathbf{g} \qquad [10]$$

where

$$\mathbf{A} = \begin{bmatrix} k\mathbf{A}_{\boldsymbol{\tau}}\big/\boldsymbol{\tau}(\boldsymbol{\lambda}_{o_i})^{(max)} \\ \hline \mathbf{A}_{\mathbf{i}}\big/I(\boldsymbol{\theta}_i)^{(max)} \end{bmatrix} \qquad [11]$$

In this case γ could be chosen according to the GCV technique (Golub et al.,1979) as the value that minimizes

$$V(\boldsymbol{\gamma}) = (n_1+n_2)\frac{\sum_{i=1}^{n_1+n_2}\left(\frac{\boldsymbol{\gamma}}{\boldsymbol{\lambda}_i+\boldsymbol{\gamma}}\right)^2 z_i^2}{\left(\sum_{i=1}^{m}\frac{\boldsymbol{\gamma}}{\boldsymbol{\lambda}_i+\boldsymbol{\gamma}} + n_1 + n_2 - m\right)^2} \qquad [12]$$

where

$[z_1 z_2 \cdots z_{(n_1+n_2)}]^T = \mathbf{U}^{\mathrm{T}}\mathbf{g}$, λ_i (i=1, ..., m) are the eigenvalues of $\mathbf{X}^{\mathrm{T}}\mathbf{X}$, $\lambda_i=0$, $i>m$. **U** is one of the matrices of the SVD of $\mathbf{X}\rightarrow\mathbf{X}=\mathbf{U}\mathbf{D}\mathbf{V}^{\mathrm{T}}$ and $\mathbf{X}=\mathbf{A}\mathbf{K}^{-1}$.

When k is unknown, as proposed here, GCV can still be used to select γ if Eq [9] is rewritten taking into account that the value of γ obtained from Eq [12] depends now also on *k*. Thus two consecutive minimization problems have to be solved to estimate $\mathbf{f}_r$ and *k*,

$$\underset{\boldsymbol{\gamma}(k)}{Min}\, V(\boldsymbol{\gamma},k) \qquad [13.a]$$

$$\underset{k,\mathbf{f}_r}{Min}\ \Phi(k,\mathbf{f}_r) = \{\left|\mathbf{g} - \mathbf{a}(k,\mathbf{f}_r)\right|^2 + \boldsymbol{\gamma}(k)\,\mathbf{f}_r^T\mathbf{H}\mathbf{f}_r\} \quad [13.b]$$

Formaly, the first problem (Eq [13.a]) is a one dimensional minimization that has to be solved repeateadly for *k* in the range of posible solutions. The result of this minimization is γ(k). For the second minimization problem (Eq [13.b]) one has to recognize that the pair *k*, $\mathbf{f}_r$ that minimizes $\Phi(k, \mathbf{f}_r)$ is a stationary point of that function, and then

$$\frac{\partial\Phi(k,\mathbf{f}_r)}{\partial\mathbf{f}_r} = 0 \quad \text{and} \quad \frac{\partial\Phi(k,\mathbf{f}_r)}{\partial k} = 0$$

From Eq[13.b] can be derived that the stationary point results in the following relations:

$$[\mathbf{A}^T\mathbf{A}+\boldsymbol{\gamma}(k)\mathbf{H}]\mathbf{f}_r-\mathbf{A}^T\mathbf{g}=0 \quad [14.a]$$

$$2\mathbf{g}_1^T\mathbf{A}_\tau\mathbf{f}_r-2k\mathbf{f}_r^T\mathbf{A}_\tau^T\mathbf{A}_\tau\mathbf{f}_r-\mathbf{f}_r^T\mathbf{H}\mathbf{f}_r\frac{d\boldsymbol{\gamma}(k)}{dk}=0 \quad [14.b]$$

Eq [14.a] can be analytically solved to give

$$\hat{\mathbf{f}}_r(k)=\left(\mathbf{A}^T\mathbf{A}+\boldsymbol{\gamma}(k)\,\mathbf{H}\right)^{-1}\mathbf{A}^T\mathbf{g} \quad [15]$$

as in the linear case, but now as a function of k through the function γ(k) calculated before. If $\mathbf{f}_r$(k) is replaced in Eq [14.b], the resulting equation has now just one unknown; i.e. k. Any method can be used to solve this equation, which result replaced in Eq [15] gives the sought solution to the inverse problem, i.e. $\mathbf{f}_r$. In practice only the values of γ(k) needed by the algorithm used to calculate k from Eqs [14.a] and [14.b] need to be evaluated, and then the computations can be performed in a single step. Each time a value of γ(k) is calculated for k, the same function must be evaluated for neighboring values of k in order to compute the derivative that appears in Eq [14.b].

In the next section the proposed methodology will be used to process synthetic data generated with Eqs [1] and [2] for different PSD's.

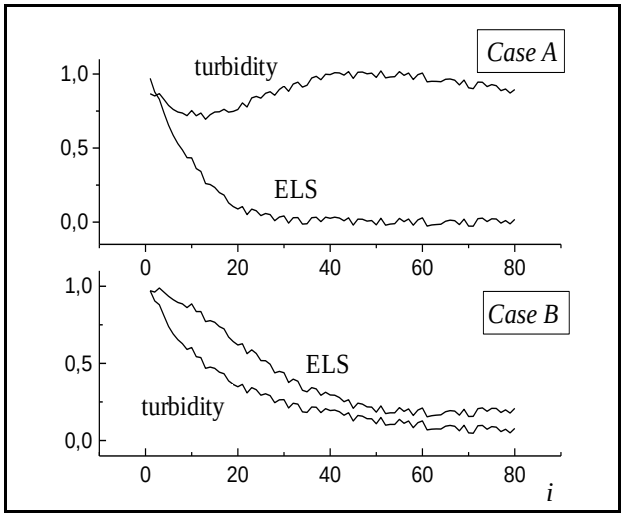

Fig.1: Normalized noisy turbidity and ELS measurements

3. Results and Dicussion

The same examples as in Eliçabe and Frontini (1996) will be used to show how the proposed methodology works in practice. Turbidity and ELS spectra were generated using lognormal distributions and combinations of them. As before the experiments were simulated for polystyrene particles in water. The spectra were generated using Eqs [5] and [6]. The PSD's were discretized in m=51 equally spaced points on the diameter axis. The parameters of the PSD's used in each example are listed in Table 1 and the corresponding spectra are shown in Figure 1. In all cases the turbidity spectra were generated using a range of wavelengths from 306 to 701 nm, with a wavelength step of 5 nm (n1=80). Data of refractive index as a function of wavelength were taken from Maron et al (1963) for water and from Inagaki et. al (1977) for polystyrene. Eighty (n2) ELS determinations were simulated for a He-Ne Laser source (λ_o=632.8 nm), in a range of angles from 12º to 150º. The refractive indexes of water and polystyrene were taken as 1.33411 and 1.58072. The generated spectra were corrupted with a 3% maximum value (relative to the maximum of the turbidity or ELS spectrum) zero-mean random noise, sampled from a uniform distribution. The label "i" for the x-axis in Figure 1 stands either for the index of the discretized wavelengths, λo_i, for turbidity measurements, or for the index of the discetized angles, θ_i, for ELS measurements.

Table 1: PSD's utilized in the simulated experiments.

DISTRIBUTION							
$f(D)=N_p^{(a)}\left[C_1/(C_1+C_2)\,LOGN_1^{(b)}+C_2/(C_1+C_2)\,LOGN_2^{(b)}\right]$							
	D_{g_1} [nm]	σ_1	D_{g_2} [nm]	σ_2	C_1	C_2	D_s [nm]
A	600	0.2	1500	0.1	2	1	0
B	175	0.2	-	-	1	0	0

$(a)N_p=8.49\times10^6[part/cm^3]$

$$(b)LOGN_i=\frac{1}{\sqrt{2\pi}\sigma_i(D-D_s)}e^{-\left[\ln(D-D_s)-\ln D_{g_i}\right]^2/2\sigma_i^2}$$

Figure 2 shows the results of recovering the PSD's of Table 1 from the noisy spectra of: turbidity, ELS, and the combination of both. The behavior of the recovered PSD's is in agreement with the qualitative analysis discussed previously for turbidity and ELS. In all the examples the distributions recovered from turbidity determinations, using Eq. [8], behave poorly at the small diameter edge, whereas at large diameters the behavior is quite correct. Oppositely, the PSD's recovered from ELS, using Eq. [9], have an excellent response at the small diameter end, and a poor response for large diameters.

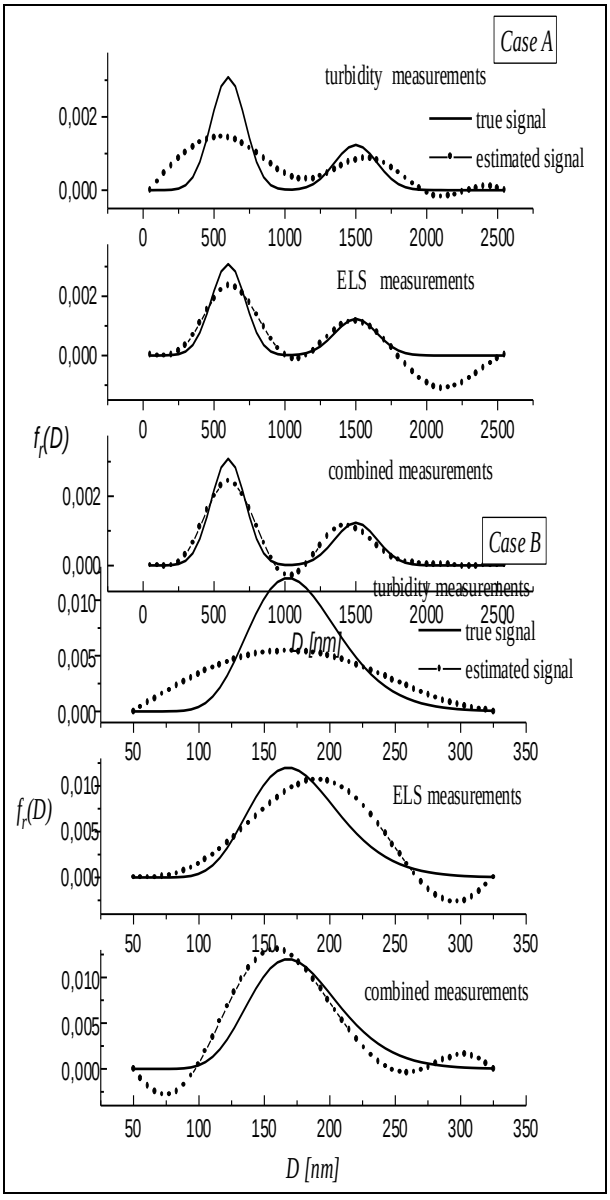

Fig. 2: Original and estimated PSD's from turbidity, ELS and turbidity-ELS spectra, for cases A and B.

The results of processing the combined experiments as proposed in Eq. [14.b] and Eq. [15] is shown in Figure 2. In all cases the recovered PSD's capture the best features of each one of the individual methods. As a result, the distributions recovered from the combined experiments present a notorious improvement with respect to any of the obtained using the individual experiments.

Conclusions

The nonlinear inverse problem resulting from the combination of a pair of indirect relative measurements was solved satisfactorily to determine the PSD of latex particles. The two techniques commonly used to independently estimate PSD's, turbidimetry and ELS, were processed at the same time to obtain a single estimation. Synthetic experiments were generated to demonstrate the convenience of processing the experimental data jointly. The information content of turbidity and ELS processed individually is highly reduced in the presence of moderated noise. Simultaneous processing increases the resolution of the recovered PSD's capturing the best features of both individual techniques. In principle, if the current technique in use is ELS, a simple additional measurement in a diode array spectrophotometer could drastically improve the quality of the obtained PSD. As far as the authors know this combination was not used before in the form and with the results exposed here.

Acknowledgments

We want to thank the financial support from CONICET and Universidad Nacional de Mar del Plata (Argentina).

References

Bohren, C. and D. Huffman, "Absorption and Scattering of Light by Small Particles," John Willey & Sons (1983).

Eliçabe, G. and G. Frontini, "Determination of the Particle Size Distribution of Latex Using a Combination of Elastic Light Scattering and Turbidimetry: A Simulation Study", *J. of Colloid and Interface Science* **181**, 669 (1996).

Eliçabe, G. and L. García-Rubio, "Latex Particle Size Distribution from Turbidimetry using inversion techniques", *J. of Colloid and Interface Science* **129**, 192 (1989).

Eliçabe, G. and L. García-Rubio, in "Polymer Characterization. Physical Property, Spectroscopic, and Chromatographic Methods" (C. Craver and T. Provder, Eds.), Advances in Chemistry Series 227, 83 (1990).

Glatter, O., M. Hofer, C. Jorde and W. Eigner, "Interpretation of Elastic Light-Scattering Data in Real Space", *J. of Colloid and Interface Science* **105**, 577 (1985).

Golub, G. H., M. Heath and G. Wahba, "Generalized Cross Validation as a Method for choosing a good Parameter", *Technometrics* **21**, 215 (1979).

Hofer, M., J. Schurz and O. Glatter, "Oil-Water Emulsions: Particle Size Distributions from Elastic Light Scattering Data."*J. of Colloid and Interface Science* **127**, 147 (1989).

Inagaki, T., E. T. Arakawa, R. N. Hamm and M. W. Williams, *Physical Review B* **15**, 3243 (1977).

Kerker, M., "The Scattering of Light and Other Electromagnetic Radiation," Academic Press, New York (1969).

Maron, S. H., P. E. Pierce and I. N. Ulevitch, *J. of Colloid Science* **18**, 470 (1963).

Phillips, D. L., "A technique for the Numerical Solution of Certain Integral Equations of the First Kind", *J. AMC* **9**, 84 (1962).

Van de Hulst, H. C., "Light Scattering by Small Particles," Dover Publications, New York (1981).